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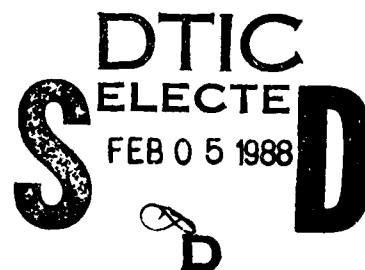
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# Computational Studies of the Reactive Properties of Some Aliphatic Diammonium Dinitrates

AD-A191 227

Peter Politzer

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NEW ORLEANS, LA 70148



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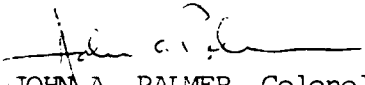
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# PREFACE

This report describes the work performed by personnel at the Department of Chemistry, University of New Orleans, New Orleans LA 70148 during the period March 1986 to September 1987. The contract program manager was Dr Peter Politzer and the AFATL program manager was Dr Robert L. McKenney Jr. Funding was provided by the Air Force Armament Laboratory, Armament Division, Energetic Materials Branch, Eglin Air Force Base, Florida 32542-5434 under Contract F08635-86-K-0112.

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# LIST OF FIGURES

Figure	Title	Page
1	Calculated Electrostatic Potential of 1,2-Diaminoethane in a Plane Passing Through the Lone Pairs of Both Nitrogens. The Projected Positions of the Nuclei, in this Plane, are Shown. Dashed Contours Correspond to Negative Potentials; all Values are in Kcal/Mole. The Positions of the Most Negative Values (Minima) in this Plane are Indicated; the Magnitudes are -41.3 Kcal/Mole, -84.6 Kcal/Mole. . . . .	24
2	Calculated Electrostatic Potential of 1,2-Diaminobutane in a Plane Passing Through the Lone Pair of One of the Nitrogens. The Projected Positions of the Nuclei, in this Plane, are Shown. Dashed Contours Correspond to Negative Potentials; all Values are in Kcal/Mole. The Position of the Most Negative Value (Minimum) in this Plane is Indicated; the Magnitude is -86.3 Kcal/Mole. The absolute Minimum in this Lone Pair Region is -96.9 Kcal/Mole. . . . .	25

# LIST OF TABLES

Table	Title	Page
1	Electrostatic Potential Minima Associated with Nitrogen Lone Pair Regions. . . . .	26

## OBJECTIVES

The objectives of this project were to determine, by computational methods, certain key properties of certain aliphatic diamines, their mono- and diprotonated forms, and some of their methyl and fluoro-derivatives. The properties to be calculated included the structures, relative bond strengths, atomic charges, and electrostatic potentials of the systems of interest. The results of the study are intended to help elucidate the thermal decomposition mechanisms of the nitrate salts of these diamines.

## SYSTEMS INVESTIGATED

A total of 22 molecules and molecular-ions were studied. These are listed on page 2. Early in the project, it was decided in consultation with Dr. Robert L. McKenney that the emphasis would be on 1,4-diaminobutane and its derivatives and protonated forms, since these compounds have been most investigated by experimental methods. Accordingly, 18 of the systems listed on page 2 are related to 1,4-diaminobutane.

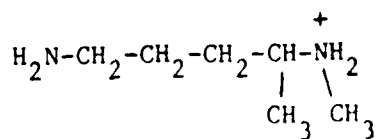
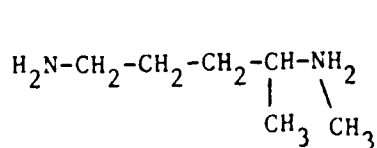
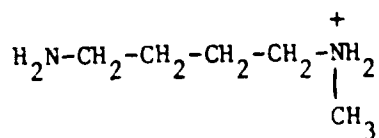
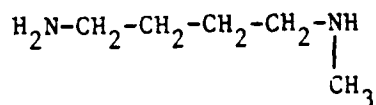
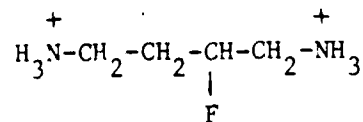
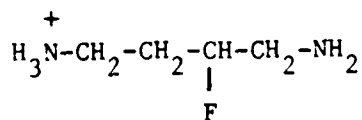
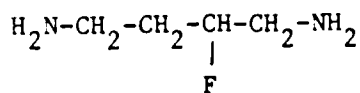
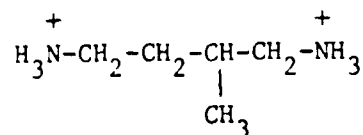
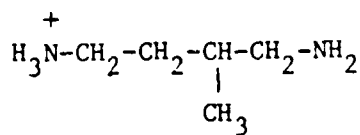
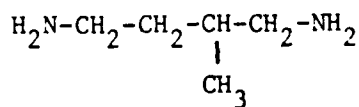
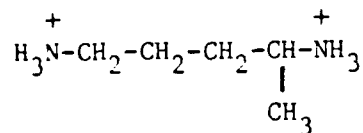
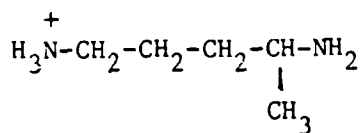
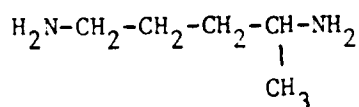
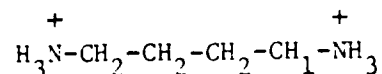
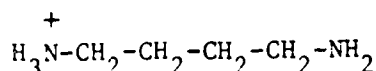
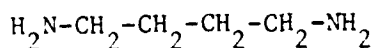
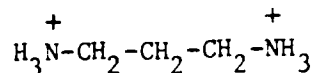
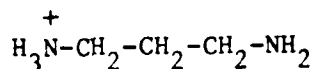
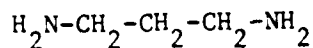
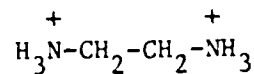
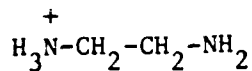
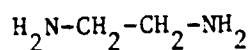
## METHODS

Our computational analyses were based on an ab initio self-consistent-field molecular orbital procedure, using the GAUSSIAN 82 system of programs [1]. The initial step was to calculate the structure of each molecule, using an optimization technique that involves computing the net force on each nucleus for each of a series of trial geometries and continually adjusting the structures until this force is zero in every case, as is required at equilibrium. The structure calculations were carried out at the 3-21G level, which has been shown to be effective for this purpose [2].

The relative bond strengths were obtained by means of a procedure that we have recently developed [3]. We showed that experimentally-determined bond dissociation energies correlate well with bond orders calculated from force constants and bond lengths by means of eq. (1):

$$\text{Bond Order} = 0.55747 (k/R_e)^{1/2} \quad (1)$$

SYSTEMS FOR WHICH COMPUTATIONAL  
STUDIES HAVE BEEN CARRIED OUT



In eq. (1),  $k$  is the force constant in mdyn/A and  $R_e$  is the equilibrium bond length in A. We obtained both of these quantities computationally, and used the resulting bond order as a measure of the relative strengths of the individual bonds in the molecules being studied.

Atomic charges were determined by the widely used population analysis procedure [4]. This is incorporated as a subroutine in the GAUSSIAN 82 program.

The electrostatic potential  $V(\hat{r})$  that is created at any point  $\hat{r}$  in the space around a molecule by its nuclei and electrons is given rigorously by eq. (2):

$$V(\hat{r}) = \sum_A \frac{Z_A}{|\hat{R}_A - \hat{r}|} - \int \frac{\rho(\hat{r}') d\hat{r}'}{|\hat{r}' - \hat{r}|} \quad (2)$$

$Z_A$  is the nuclear charge on atom A, located at  $\hat{R}_A$ , and  $\rho(\hat{r})$  is the molecular electronic density function, which we obtain computationally.

The electrostatic potential is an effective means for interpreting and predicting chemical reactive behavior, especially toward electrophiles [5-7]. Eq. (2) shows that  $V(\hat{r})$  is negative in those regions in which the effects of the molecule's electrons are dominant, and it is to these regions that an approaching electrophile is initially attracted, especially to those points at which  $V(\hat{r})$  attains its most negative values (local minima).

An important feature of the electrostatic potential is that it is a real physical property, and can be determined experimentally, by diffraction methods [7], as well as computationally. The physical reality of  $V(\hat{r})$  stands in contrast to the unavoidable arbitrariness associated with many other indices of reactivity.

We calculated the atomic charges and electrostatic potentials in terms of the STO-5G basis set, which we have found to give reliable results for these properties. The bond orders were computed at the STO-3G level. The use of this smaller basis was dictated by the time- and space-consuming requirements of the necessary force constant calculations. We have shown, however, that STO-3G bond orders show the same trends as those obtained with larger basis sets.



## RESULTS

On pages 9 through 23 are presented the calculated structures, bond orders and atomic charges of the systems listed on page 2. Figures 1 and 2, on pages 24 and 25, show electrostatic potential plots for 1,2-diaminoethane and 1,4-diaminobutane. Finally, Table 1 (page 26) gives the most negative values (minima) of the electrostatic potentials in the nitrogen lone pair regions of six of the neutral diamines that were studied in this project. It should be noted that the minima shown in Figures 1 and 2 are not the same as those in Table 1. This is because the latter are the absolute minima in the lone pair regions, whereas the former refer only to the planes indicated.

## SUMMARY OF RESULTS

### A. Effects of Protonation on Unsubstituted 1,2-Diaminoethane, 1,3-Diaminopropane and 1,4-Diaminobutane: (Rows 1 - 3 on page 2.)

#### 1. Structures:

Protonation of a nitrogen causes the corresponding C-N bond to lengthen by about 0.07 Å. The N-H bonds also become longer, but only by about 0.02 Å. An interesting special case is 1,2-diaminoethane, for which one N-H bond length increases to 1.06 Å, while the C-N-H angle changes to  $100^\circ$  rather than being in the more customary neighborhood of  $113^\circ$ .

#### 2. Bond Orders:

Consistent with the above bond length changes, the C-N bond to the protonated nitrogen is weakened by about 0.2 units, while the N-H bonds become slightly weaker. An exception again is one N-H bond, for which the bond order diminishes to 1.40. The C-H bonds, in general, become slightly stronger as the nitrogens are protonated.

#### 3. Atomic Charges:

Protonation of the nitrogens causes both the carbons and the nitrogens to become more negative, the effect being less for the latter. The hydrogens throughout the molecule become more positive, especially those

on the protonated nitrogen. Thus the overall positive charge of the system is delocalized to the hydrogens. Those on the carbon adjacent to the protonated nitrogen are more positive than those on the other carbons.

B. Effects of Substituents on 1,4-Diaminobutane:

1. Methyl Group on C<sub>4</sub>:

Methylation causes C<sub>4</sub> to be less negative, by roughly 0.1 unit, than in the unsubstituted molecule. Protonation of the attached nitrogen makes the C<sub>4</sub>-N bond slightly weaker when C<sub>4</sub> is methylated than in the absence of the methyl group. The CH<sub>3</sub> group acts as an electron donor to the system, and has a net positive charge. This is less positive, however, than was the hydrogen that it replaced.

2. Methyl Group on C<sub>3</sub>:

Methylation causes C<sub>3</sub> to be less negative, by roughly 0.1 unit, than in the unsubstituted molecule. Again, the CH<sub>3</sub> acts as an electron donor, but is less positive than the hydrogen that it replaced.

3. Fluorine on C<sub>3</sub>:

The substitution of fluorine on C<sub>3</sub> causes the carbon to become positively charged, while the neighboring carbons become somewhat more negative. The hydrogens in general become slightly more positive. The presence of the fluorine causes the adjacent C-C bonds and the C-N bonds to become somewhat shorter and stronger.

4. Methyl Group on N<sub>2</sub>:

When a nitrogen is methylated, the CH<sub>3</sub> acts as an electron donor and is approximately as positive as the hydrogen that it replaced. The methyl carbon is about 0.15 units less negative than the carbons of CH<sub>3</sub> groups substituted on C<sub>1</sub> - C<sub>4</sub>. In the neutral diamine, the methylated nitrogen is less negative by 0.07 than when it is not methylated. Upon protonation, this nitrogen attains a charge of -0.80, which is what it normally has in neutral systems when it is not methylated. The C<sub>4</sub>-N<sub>2</sub> bond, for methylated N<sub>2</sub>, is not weakened quite as much by protonation of

$N_2$  as it is in the absence of methylation. The  $N_2$ -methyl bond, for protonated  $N_2$ , is significantly stronger than we have previously found for C-N bonds when the nitrogen is protonated.

5. Methyl Groups on Both  $C_4$  and  $N_2$ :

Both methyl groups act as electron donors; however only the one on the nitrogen is as positive as the hydrogen that was replaced. The  $N_2$ -methyl bond is again significantly stronger than ordinarily found for C-N bonds to protonated nitrogens; however the  $C_4$ - $N_2$  bond is now weakened as much as usual. In the neutral diamine, both nitrogens are only about half as negative as usual. However upon protonation of  $N_2$ , both charges change to their customary neutral system values.

6. General Observation for Substituted 1,4-Diaminobutanes:

Superposed upon the effects that have been summarized above are the trends that were noted earlier for the unsubstituted systems in going from the neutral to the mono-protonated to the di-protonated forms.

C. Electrostatic Potentials:

Figures 1 and 2, on pages 24 and 25, show that there are strong and extended regions of negative potential associated with the nitrogens in the neutral diamines. These can be attributed to the effects of their lone pairs. Table 1 (page 26) lists the values of the absolute minima (the most negative points) in these regions for six of the neutral molecules. Electrostatic potentials have not been computed for the protonated molecules, since our experience has been (and was confirmed for one of the present cases) that the potentials of positively-charged systems show no negative regions anywhere, and are relatively uninformative.

The nitrogen negative potentials in all of these diamines are weaker than is that due to the highly-localized lone pair of ammonia. For the nitrogens that are at least three carbons away from any substituent, the minima are in the range -95 to -99 kcal/mole. In the molecules that are methylated on  $C_3$  or  $C_4$ , the  $N(C_4)$  minimum is slightly more negative, consistent with the weakly electron-donating nature of the methyl group. This is not observed, however, in the molecule that is methylated on

both  $C_4$  and  $N(C_4)$ ; the nitrogen minimum is only -98.9 kcal/mole, which may reflect positive contributions from hydrogens on the two methyl groups that are in such close proximity. Similarly, the minimum observed for the fluorinated diamine may include some negative contribution from the fluorine.

### CONCLUSIONS

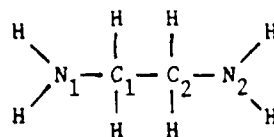
- (1) The protonation of a nitrogen causes its bond to the terminal carbon of the chain to become considerably weaker. The weakening is even more pronounced when the terminal carbon is methylated.
- (2) The positive charge of the protonated systems is spread out over the hydrogens; the carbons and nitrogens are actually more negative than in the neutral molecules.
- (3) Methylation of the carbon chain causes the nearer of the amine nitrogens to become significantly more basic, as evidenced by its more negative electrostatic potential.
- (4) Substitution of a fluorine strengthens the adjacent C-C and the C-N bonds.
- (5) When an amine nitrogen is methylated, its bond to the terminal carbon of the chain is not weakened by protonation to as great an extent as in the absence of the methyl group. The bond from the protonated nitrogen to the methyl carbon is significantly stronger than the bonds from protonated nitrogens to terminal carbons.

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Calculated Properties of 1,2-Diaminoethane and Its Mono-  
and Diprotonated Forms

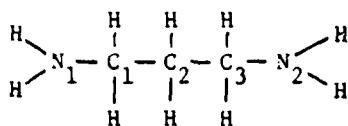


Distance (Å) or Angle (deg)	Neutral Molecule	N <sub>1</sub> Protonated	N <sub>1</sub> and N <sub>2</sub> Protonated
C <sub>1</sub> -C <sub>2</sub>	1.531	1.551	1.546
C <sub>1</sub> -N <sub>1</sub>	1.476	1.532	1.549
C <sub>2</sub> -N <sub>2</sub>	1.467	1.484	1.548
C-H	1.09 (ave)	1.08 (ave)	1.08 (ave)
N-H	1.00 (ave)	N-H: 1.01 (ave) N <sub>1</sub> -H <sup>+</sup> : 1.06	1.02 (ave)
N <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub>	109	105	113
H-N <sub>1</sub> -C <sub>1</sub>	114 (ave)	113 (ave) H <sup>+</sup> -N <sub>1</sub> -C <sub>1</sub> : 100	109 - 114
H-N <sub>2</sub> -C <sub>2</sub>	110, 114	113, 114	109 - 112

Bond Order	Neutral Molecule	N <sub>1</sub> Protonated	N <sub>1</sub> and N <sub>2</sub> Protonated
C <sub>1</sub> -C <sub>2</sub>	1.16	1.14	1.12
C <sub>1</sub> -N <sub>1</sub>	1.25	1.10	1.06
C <sub>2</sub> -N <sub>2</sub>	1.27	1.24	1.06
N-H	1.78	N-H: 1.76 (ave) N <sub>1</sub> -H <sup>+</sup> : 1.40	1.69 - 1.72
C-H	1.43 - 1.49	1.50 - 1.52	1.51

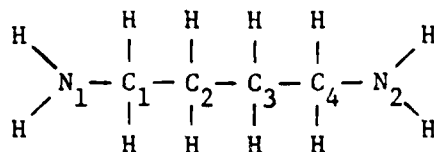
Atomic Charge	Neutral Molecule	N <sub>1</sub> Protonated	N <sub>1</sub> and N <sub>2</sub> Protonated
C <sub>1</sub>	-0.21	-0.26	-0.29
C <sub>2</sub>	-0.18	-0.25	-0.29
N <sub>1</sub>	-0.80	-0.86	-0.84
N <sub>2</sub>	-0.80	-0.84	-0.84
H(C <sub>1</sub> )	0.18, 0.23	0.30	0.34, 0.38
H(C <sub>2</sub> )	0.16, 0.20	0.27, 0.28	0.34, 0.38
H(N <sub>1</sub> )	0.30	0.43 - 0.48	0.45 - 0.48
H(N <sub>2</sub> )	0.29, 0.32	0.36, 0.37	0.45 - 0.48

Calculated Properties of 1,2-Diaminopropane and Its Mono- and Diprotonated Forms



Property	Neutral Molecule	N <sub>1</sub> Protonated	N <sub>1</sub> and N <sub>2</sub> Protonated
Distance (Å) or Angle (deg):			
C <sub>1</sub> -C <sub>2</sub>	1.544	1.536	1.545
C <sub>2</sub> -C <sub>3</sub>	1.541	1.540	1.544
C <sub>1</sub> -N <sub>1</sub>	1.470	1.538	1.547
C <sub>3</sub> -N <sub>2</sub>	1.474	1.507	1.547
C-H	1.09 (ave)	1.08 (ave)	1.08 (ave)
N <sub>1</sub> -H	1.00 (ave)	1.01, 1.01, 1.09	1.02 (ave)
N <sub>2</sub> -H	1.00 (ave)	1.01 (ave)	1.02 (ave)
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	114	112	109
N <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub>	109	108	111
N <sub>2</sub> -C <sub>3</sub> -C <sub>2</sub>	111	110	111
H-N <sub>1</sub> -C <sub>1</sub>	115 (ave)	103, 111, 112	110 - 112
H-N <sub>2</sub> -C <sub>3</sub>	114	112	110 - 112
Bond Order:			
C <sub>1</sub> -C <sub>2</sub>	1.12	1.18	1.11
C <sub>2</sub> -C <sub>3</sub>	1.14	1.18	1.12
N <sub>1</sub> -C <sub>1</sub>	1.26	1.13	1.06
N <sub>2</sub> -C <sub>3</sub>	1.25	1.19	1.06
C-H	1.43 - 1.48	1.47 - 1.51	1.47 - 1.51
N-H	1.78 - 1.80	1.71 - 1.76	1.71 - 1.72
Atomic Charge:			
C <sub>1</sub>	-0.18	-0.25	-0.25
C <sub>2</sub>	-0.45	-0.47	-0.50
C <sub>3</sub>	-0.19	-0.23	-0.25
N <sub>1</sub>	-0.81	-0.88	-0.83
N <sub>2</sub>	-0.79	-0.85	-0.83
H(C <sub>1</sub> )	0.21, 0.22	0.29	0.33
H(C <sub>2</sub> )	0.20, 0.23	0.25, 0.29	0.29
H(C <sub>3</sub> )	0.17, 0.22	0.26, 0.27	0.33
H(N <sub>1</sub> )	0.30	0.41 - 0.50	0.41 - 0.46
H(N <sub>2</sub> )	0.29	0.35, 0.36	0.46 - 0.47

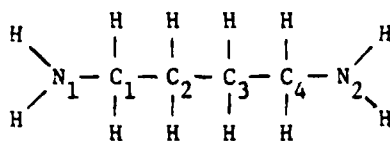
Calculated Structures of 1,4-Diaminobutane and Its Mono- and  
Diprotonated Forms



Distance (A) or Angle (deg)	Neutral Molecule	N <sub>1</sub> Protonated	N <sub>1</sub> and N <sub>2</sub> Protonated
C <sub>1</sub> -C <sub>2</sub>	1.537	1.530	1.539
C <sub>2</sub> -C <sub>3</sub>	1.537	1.541	1.552
C <sub>3</sub> -C <sub>4</sub>	1.541	1.541	1.541
C <sub>1</sub> -N <sub>1</sub>	1.474	1.559	1.557
C <sub>4</sub> -N <sub>2</sub>	1.474	1.465	1.565
C-H	1.09 (ave)	1.08 (ave)	1.08 (ave)
N-H	1.00 (ave)	N <sub>1</sub> -H: 1.02 (ave) N <sub>2</sub> -H: 1.00 (ave)	1.02 (ave)
N <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub>	110	110	112
N <sub>2</sub> -C <sub>4</sub> -C <sub>3</sub>	115	109	111
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	112	113	115
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	112	112	109
H-N-C	113 (ave)	H-N <sub>1</sub> -C <sub>1</sub> : 111 (ave) H-N <sub>2</sub> -C <sub>4</sub> : 115	111 (ave)



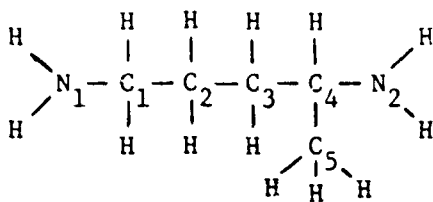
Calculated Properties of 1,4-Diaminobutane and Its Mono- and Diprotonated Forms



Bond Order	Neutral Molecule	N <sub>1</sub> Protonated	N <sub>1</sub> and N <sub>2</sub> Protonated
C <sub>1</sub> -C <sub>2</sub>	1.15	1.14	1.12
C <sub>2</sub> -C <sub>3</sub>	1.14	1.13	1.10
C <sub>3</sub> -C <sub>4</sub>	1.12	1.13	1.12
C <sub>1</sub> -N <sub>1</sub>	1.25	1.01	1.03
C <sub>4</sub> -N <sub>2</sub>	1.25	1.28	1.03
C-H	1.44-1.48	1.46-1.51	1.47-1.51
N-H	1.77-1.78	N <sub>1</sub> -H: 1.74 N <sub>2</sub> -H: 1.79	1.72-1.74

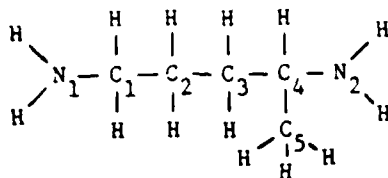
Atomic Charge	Neutral Molecule	N <sub>1</sub> Protonated	N <sub>1</sub> and N <sub>2</sub> Protonated
C <sub>1</sub>	-0.19	-0.26	-0.26
C <sub>2</sub>	-0.42	-0.47	-0.47
C <sub>3</sub>	-0.43	-0.43	-0.48
C <sub>4</sub>	-0.19	-0.17	-0.23
N <sub>1</sub>	-0.79	-0.83	-0.83
N <sub>2</sub>	-0.78	-0.80	-0.85
H(C <sub>1</sub> )	0.18, 0.21	0.30	0.32, 0.34
H(C <sub>2</sub> )	0.20	0.24, 0.28	0.27, 0.31
H(C <sub>3</sub> )	0.19, 0.24	0.21, 0.23	0.24, 0.27
H(C <sub>4</sub> )	0.21	0.21, 0.23	0.32
H(N <sub>1</sub> )	0.29, 0.30	0.44-0.45	0.45-0.46
H(N <sub>2</sub> )	0.29	0.31, 0.32	0.45-0.46

Calculated Structures of 1,4-Diamino-4-methylbutane and Its Mono-  
and Diprotonated Forms



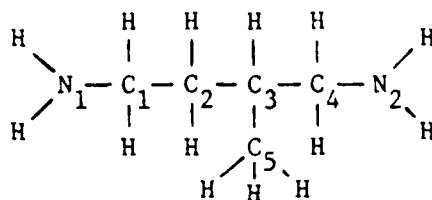
Distance (A) or Angle (deg)	Neutral Molecule	N <sub>1</sub> Protonated	N <sub>1</sub> and N <sub>2</sub> Protonated
C <sub>1</sub> -C <sub>2</sub>	1.537	1.531	1.538
C <sub>2</sub> -C <sub>3</sub>	1.537	1.543	1.552
C <sub>3</sub> -C <sub>4</sub>	1.543	1.557	1.544
C <sub>4</sub> -C <sub>5</sub>	1.535	1.536	1.531
C <sub>1</sub> -N <sub>1</sub>	1.474	1.560	1.556
C <sub>4</sub> -N <sub>2</sub>	1.480	1.454	1.565
C-H	1.09 (ave)	1.08 (ave)	1.08 (ave)
N <sub>1</sub> -H	1.00 (ave)	1.02 (ave)	1.02 (ave)
N <sub>2</sub> -H	1.01 (ave)	1.00 (ave)	1.02 (ave)
N <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub>	110	110	112
N <sub>2</sub> -C <sub>4</sub> -C <sub>3</sub>	112	112	108
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	112	113	115
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	114	113	111
C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	112	112	115
H-N <sub>1</sub> -C <sub>1</sub>	114 (ave)	110 (ave)	111 (ave)
H-N <sub>2</sub> -C <sub>4</sub>	113 (ave)	117 (ave)	111 (ave)

Calculated Properties of 1,4-Diamino-4-methylbutane and Its Mono-  
and Diprotonated Forms



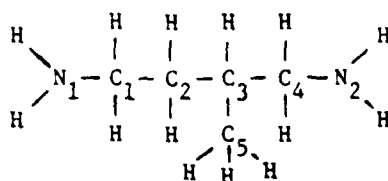
Property	Neutral Molecule	N <sub>1</sub> Protonated	N <sub>1</sub> and N <sub>2</sub> Protonated
Bond Order:			
C <sub>1</sub> -C <sub>2</sub>	1.14	1.14	1.12
C <sub>2</sub> -C <sub>3</sub>	1.14	1.12	1.10
C <sub>3</sub> -C <sub>4</sub>	1.12	1.08	1.12
C <sub>4</sub> -C <sub>5</sub>	1.15	1.14	1.14
C <sub>1</sub> -N <sub>1</sub>	1.25	1.01	1.03
C <sub>4</sub> -N <sub>2</sub>	1.24	1.30	1.00
C-H	1.47 (ave)	1.47 (ave)	1.48 (ave)
N <sub>1</sub> -H	1.77	1.74	1.73 (ave)
N <sub>2</sub> -H	1.77	1.80	1.73 (ave)
Atomic Charge:			
C <sub>1</sub>	-0.19	-0.26	-0.26
C <sub>2</sub>	-0.43	-0.47	-0.47
C <sub>3</sub>	-0.39	-0.43	-0.44
C <sub>4</sub>	-0.07	-0.03	-0.12
C <sub>5</sub>	-0.56	-0.57	-0.61
N <sub>1</sub>	-0.79	-0.83	-0.83
N <sub>2</sub>	-0.77	-0.80	-0.82
H(C <sub>1</sub> )	0.18, 0.21	0.30	0.32, 0.34
H(C <sub>2</sub> )	0.20	0.25, 0.28	0.27, 0.30
H(C <sub>3</sub> )	0.19, 0.23	0.18, 0.28	0.24, 0.26
H(C <sub>4</sub> )	0.22	0.24	0.32
H(N <sub>1</sub> )	0.29, 0.30	0.44 - 0.45	0.44 - 0.46
H(N <sub>2</sub> )	0.22, 0.29	0.31, 0.32	0.44 - 0.46
H(C <sub>5</sub> )	0.19 - 0.22	0.19 - 0.26	0.25 - 0.28

Calculated Structures of 1,4-Diamino-3-methylbutane and Its Mono-  
and Diprotonated Forms



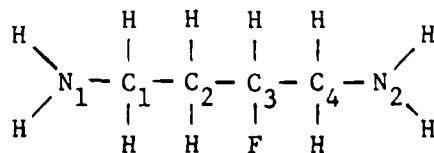
Distance (A) or Angle (deg)	Neutral Molecule	N <sub>1</sub> Protonated	N <sub>1</sub> and N <sub>2</sub> Protonated
C <sub>1</sub> -C <sub>2</sub>	1.540	1.535	1.548
C <sub>2</sub> -C <sub>3</sub>	1.545	1.545	1.554
C <sub>3</sub> -C <sub>4</sub>	1.548	1.547	1.544
C <sub>3</sub> -C <sub>5</sub>	1.538	1.538	1.541
C <sub>1</sub> -N <sub>1</sub>	1.475	1.559	1.556
C <sub>4</sub> -N <sub>2</sub>	1.470	1.464	1.553
C-H	1.09 (ave)	1.08 (ave)	1.08 (ave)
N <sub>1</sub> -H	1.01 (ave)	1.02 (ave)	1.02 (ave)
N <sub>2</sub> -H	1.00 (ave)	1.00 (ave)	1.02 (ave)
N <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub>	112	111	112
N <sub>2</sub> -C <sub>4</sub> -C <sub>3</sub>	116	110	112
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	115	115	114
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	109	109	107
C <sub>2</sub> -C <sub>3</sub> -C <sub>5</sub>	112	114	112
H-N <sub>1</sub> -C <sub>1</sub>	113	110 (ave)	111 (ave)
H-N <sub>2</sub> -C <sub>4</sub>	114	115 (ave)	111 (ave)

Calculated Properties of 1,4-Diamino-3-methylbutane and Its Mono-  
and Diprotonated Forms



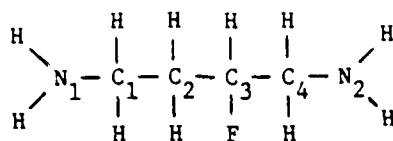
Property	Neutral Molecule	N <sub>1</sub> Protonated	N <sub>1</sub> and N <sub>2</sub> Protonated
Bond Order:			
C <sub>1</sub> -C <sub>2</sub>	1.14	1.13	1.11
C <sub>2</sub> -C <sub>3</sub>	1.13	1.12	1.10
C <sub>3</sub> -C <sub>4</sub>	1.11	1.12	1.11
C <sub>3</sub> -C <sub>5</sub>	1.14	1.13	1.13
C <sub>1</sub> -N <sub>1</sub>	1.25	1.01	1.03
C <sub>4</sub> -N <sub>2</sub>	1.26	1.28	1.04
C-H	1.46 (ave)	1.47 (ave)	1.49 (ave)
N <sub>1</sub> -H	1.77 (ave)	1.74 (ave)	1.73 (ave)
N <sub>2</sub> -H	1.78 (ave)	1.79 (ave)	1.73 (ave)
Atomic Charge:			
C <sub>1</sub>	-0.19	-0.26	-0.26
C <sub>2</sub>	-0.39	-0.44	-0.44
C <sub>3</sub>	-0.31	-0.30	-0.36
C <sub>4</sub>	-0.15	-0.15	-0.22
C <sub>5</sub>	-0.58	-0.62	-0.60
N <sub>1</sub>	-0.78	-0.84	-0.84
N <sub>2</sub>	-0.80	-0.80	-0.84
H(C <sub>1</sub> )	0.18, 0.22	0.30	0.32, 0.34
H(C <sub>2</sub> )	0.20	0.23, 0.28	0.26, 0.30
H(C <sub>3</sub> )	0.20	0.24	0.27
H(C <sub>4</sub> )	0.20	0.21, 0.28	0.31, 0.45
H(N <sub>1</sub> )	0.29, 0.30	0.44 - 0.46	0.45 - 0.46
H(N <sub>2</sub> )	0.29, 0.30	0.32, 0.33	0.45 - 0.46
H(C <sub>5</sub> )	0.17 - 0.26	0.16 - 0.31	0.23 - 0.24

Calculated Structures of 1,4-Diamino-3-fluorobutane and Its Mono-  
and Diprotonated Forms



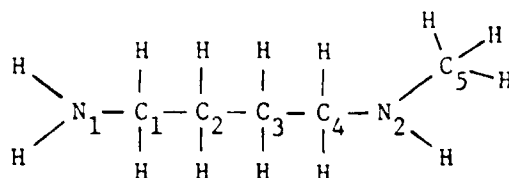
Distance (Å) or Angle (deg)	Neutral Molecule	N <sub>1</sub> Protonated	N <sub>1</sub> and N <sub>2</sub> Protonated
C <sub>1</sub> -C <sub>2</sub>	1.541	1.535	1.539
C <sub>2</sub> -C <sub>3</sub>	1.523	1.527	1.528
C <sub>3</sub> -C <sub>4</sub>	1.526	1.517	1.527
C <sub>1</sub> -N <sub>1</sub>	1.466	1.549	1.548
C <sub>4</sub> -N <sub>2</sub>	1.467	1.458	1.541
C-H	1.08 (ave)	1.08 (ave)	1.08 (ave)
N-H	1.00 (ave)	N <sub>1</sub> -H: 1.02 (ave) N <sub>2</sub> -H: 1.00 (ave)	1.02 (ave)
C <sub>3</sub> -F	1.430	1.454	1.436
N <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub>	110	109	111
N <sub>2</sub> -C <sub>4</sub> -C <sub>3</sub>	113	108	108
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	113	113	113
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	114	115	113
C <sub>2</sub> -C <sub>3</sub> -F	107	107	108
H-N <sub>1</sub> -C <sub>1</sub>	115 (ave)	106-112	110 (ave)
H-N <sub>2</sub> -C <sub>4</sub>	113 (ave)	114-116	111 (ave)

Calculated Properties of 1,4-Diamino-3-fluorobutane and Its Mono-  
and Diprotonated Forms



Property	Neutral Molecule	N <sub>1</sub> Protonated	N <sub>1</sub> and N <sub>2</sub> Protonated
Bond Order:			
C <sub>1</sub> -C <sub>2</sub>	1.15	1.14	1.13
C <sub>2</sub> -C <sub>3</sub>	1.18	1.18	1.16
C <sub>3</sub> -C <sub>4</sub>	1.16	1.18	1.16
C <sub>1</sub> -N <sub>1</sub>	1.28	1.06	1.06
C <sub>4</sub> -N <sub>2</sub>	1.27	1.30	1.07
C <sub>3</sub> -F	1.29	1.22	1.27
C-H	1.47 (ave)	1.49 (ave)	1.50 (ave)
N <sub>1</sub> -H	1.80 (ave)	1.60-1.75	1.72 (ave)
N <sub>2</sub> -H	1.78 (ave)	1.79 (ave)	1.72 (ave)
Atomic Charge:			
C <sub>1</sub>	-0.16	-0.26	-0.26
C <sub>2</sub>	-0.50	-0.52	-0.52
C <sub>3</sub>	0.17	0.15	0.13
C <sub>4</sub>	-0.23	-0.22	-0.28
N <sub>1</sub>	-0.82	-0.86	-0.85
N <sub>2</sub>	-0.78	-0.80	-0.84
F	-0.41	-0.41	-0.39
H(C <sub>1</sub> )	0.19, 0.21	0.30, 0.31	0.32, 0.35
H(C <sub>2</sub> )	0.22, 0.24	0.26, 0.30	0.29, 0.33
H(C <sub>3</sub> )	0.23	0.28	0.30
H(C <sub>4</sub> )	0.22, 0.24	0.22, 0.25	0.34
H(N <sub>1</sub> )	0.30, 0.33	0.43-0.48	0.45-0.46
H(N <sub>2</sub> )	0.29, 0.32	0.33	0.46-0.47

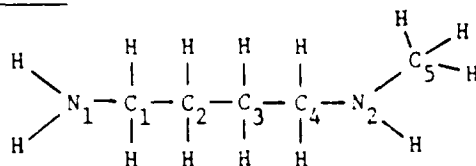
Calculated Structures of 1,4-Diamino-N-methylbutane and Its Mono-Protonated Form



Distance (A) or Angle (deg)	Neutral Molecule	N <sub>2</sub> Protonated
C <sub>1</sub> -C <sub>2</sub>	1.537	1.540
C <sub>2</sub> -C <sub>3</sub>	1.537	1.542
C <sub>3</sub> -C <sub>4</sub>	1.534	1.528
C <sub>1</sub> -N <sub>1</sub>	1.472	1.474
C <sub>4</sub> -N <sub>2</sub>	1.468	1.546
N <sub>2</sub> -C <sub>5</sub>	1.465	1.524
C-H	1.09 (ave)	1.08 (ave)
N <sub>1</sub> -H	1.00 (ave)	1.00 (ave)
N <sub>2</sub> -H	1.00	1.02 (ave)
N <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub>	110	109
N <sub>2</sub> -C <sub>4</sub> -C <sub>3</sub>	110	110
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	112	110
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	112	111
C <sub>4</sub> -N <sub>2</sub> -C <sub>5</sub>	115	113
H-N <sub>1</sub> -C <sub>1</sub>	114 (ave)	113 (ave)
H-N <sub>2</sub> -C <sub>4</sub>	112 (ave)	108 (ave)

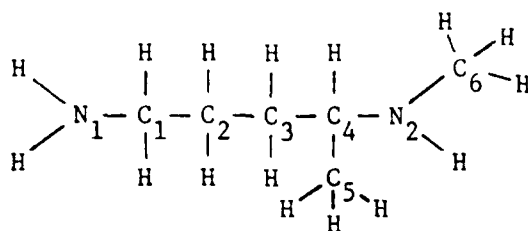


Calculated Properties of 1,4-Diamino-N-methylbutane and Its Mono-Protonated Form



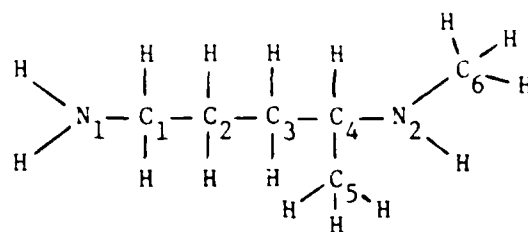
Property	Neutral Molecule	N <sub>2</sub> Protonated
Bond Order:		
C <sub>1</sub> -C <sub>2</sub>	1.15	1.14
C <sub>2</sub> -C <sub>3</sub>	1.14	1.13
C <sub>3</sub> -C <sub>4</sub>	1.15	1.14
C <sub>1</sub> -N <sub>1</sub>	1.26	1.26
C <sub>4</sub> -N <sub>2</sub>	1.27	1.06
N <sub>2</sub> -C <sub>5</sub>	1.28	1.13
C-H	1.46 (ave)	1.48 (ave)
N <sub>1</sub> -H	1.78 (ave)	1.77 (ave)
N <sub>2</sub> -H	1.77	1.74 (ave)
Atomic Charge:		
C <sub>1</sub>	-0.19	-0.20
C <sub>2</sub>	-0.42	-0.42
C <sub>3</sub>	-0.41	-0.46
C <sub>4</sub>	-0.16	-0.24
N <sub>1</sub>	-0.79	-0.80
N <sub>2</sub>	-0.73	-0.80
C <sub>5</sub>	-0.37	-0.43
H(C <sub>1</sub> )	0.18, 0.20	0.22, 0.23
H(C <sub>2</sub> )	0.20	0.22, 0.23
H(C <sub>3</sub> )	0.19, 0.26	0.23, 0.28
H(C <sub>4</sub> )	0.16, 0.20	0.29
H(N <sub>1</sub> )	0.29, 0.30	0.31, 0.32
H(N <sub>2</sub> )	0.30	0.43
H(C <sub>5</sub> )	0.16 - 0.20	0.29

Calculated Structures of 1,4-Diamino-4-methyl-N(4)-methylbutane and  
Its Monoprotonated Form



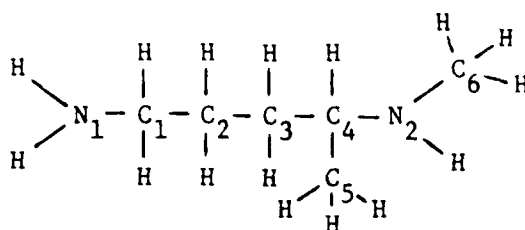
Distance (A) or Angle (deg)	Neutral Molecule	N <sub>2</sub> Protonated
C <sub>1</sub> -C <sub>2</sub>	1.537	1.540
C <sub>2</sub> -C <sub>3</sub>	1.537	1.541
C <sub>3</sub> -C <sub>4</sub>	1.539	1.534
C <sub>4</sub> -C <sub>5</sub>	1.536	1.529
C <sub>1</sub> -N <sub>1</sub>	1.472	1.474
C <sub>4</sub> -N <sub>2</sub>	1.476	1.564
N <sub>2</sub> -C <sub>6</sub>	1.466	1.522
C-H	1.08 - 1.09	1.08 (ave)
N <sub>1</sub> -H	1.00 - 1.05	1.00 (ave)
N <sub>2</sub> -H	1.005	1.02 (ave)
N <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub>	110	109
N <sub>2</sub> -C <sub>4</sub> -C <sub>3</sub>	108	107
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	112	110
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	114	113
C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	112	114
C <sub>4</sub> -N <sub>2</sub> -C <sub>6</sub>	116	115
H-N <sub>1</sub> -C <sub>1</sub>	113, 114	114 (ave)
H-N <sub>2</sub> -C <sub>4</sub>	112	108 (ave)

Calculated Bond Orders of 1,4-Diamino-4-methyl-N(4)-methylbutane and  
Its Monoprotonated Form

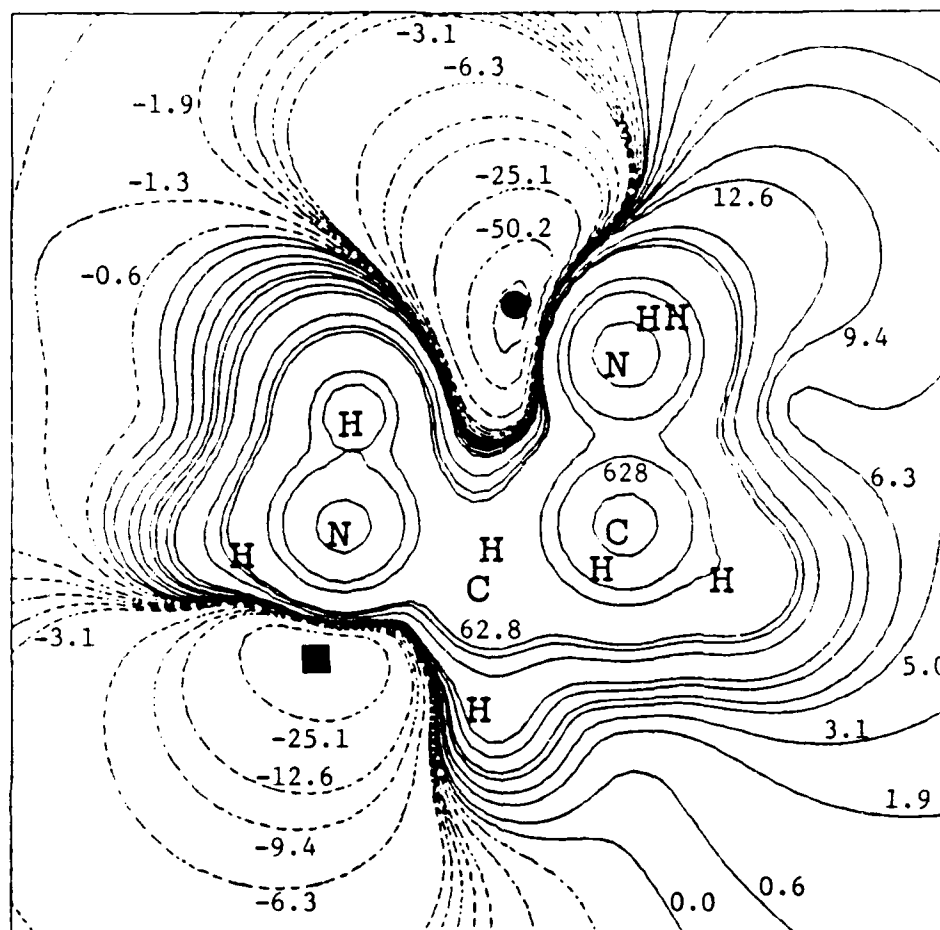


Bond	Neutral Molecule	N <sub>2</sub> Protonated
C <sub>1</sub> -C <sub>2</sub>	1.15	1.14
C <sub>2</sub> -C <sub>3</sub>	1.14	1.13
C <sub>3</sub> -C <sub>4</sub>	1.14	1.14
C <sub>4</sub> -C <sub>5</sub>	1.14	1.15
C <sub>1</sub> -N <sub>1</sub>	1.26	1.25
C <sub>4</sub> -N <sub>2</sub>	1.25	1.01
N <sub>2</sub> -C <sub>6</sub>	1.27	1.14
C-H	1.43 - 1.49	1.45 - 1.52
N <sub>1</sub> -H	1.77, 1.78	1.77, 1.78
N <sub>2</sub> -H	1.77	1.74

Calculated Atomic Charges in 1,4-Diamino-4-methyl-N(4)-methylbutane  
and Its Monoprotonated Form



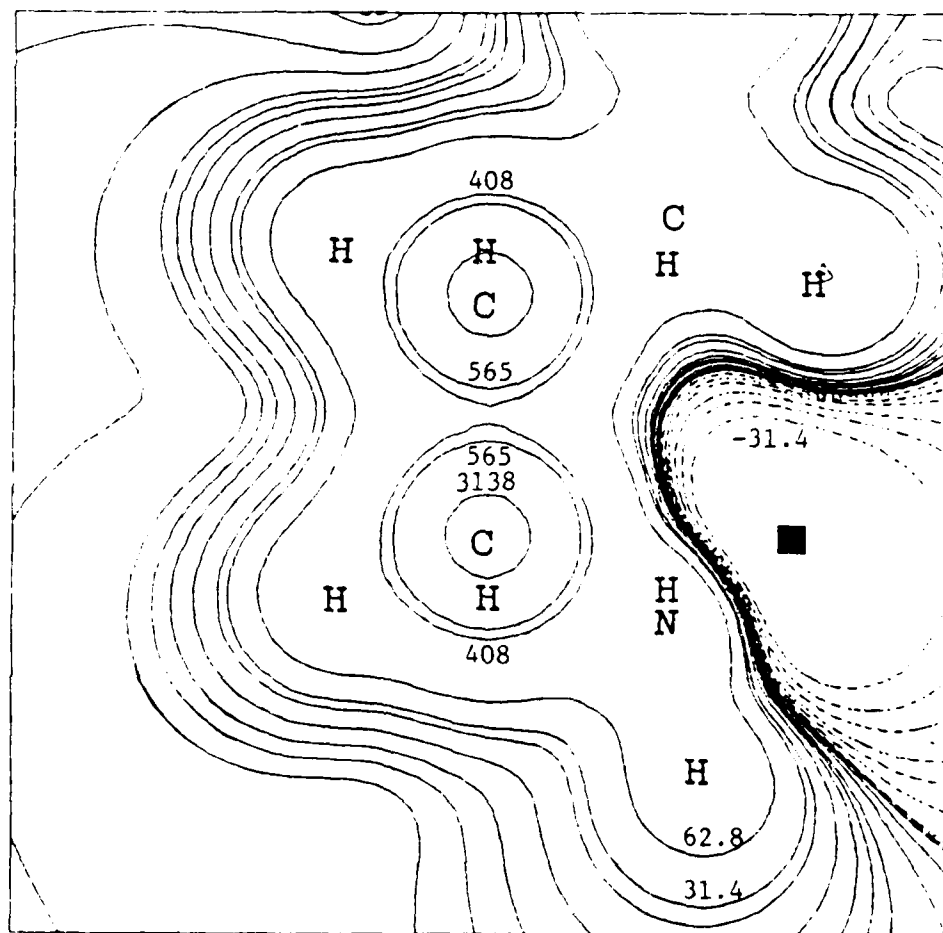
Atom	Neutral Molecule	N <sub>2</sub> Protonated
C <sub>1</sub>	-0.01	-0.20
C <sub>2</sub>	-0.10	-0.43
C <sub>3</sub>	-0.10	-0.42
C <sub>4</sub>	0.07	-0.11
C <sub>5</sub>	-0.19	-0.60
C <sub>6</sub>	-0.09	-0.43
N <sub>1</sub>	-0.44	-0.80
N <sub>2</sub>	-0.36	-0.79
H(C <sub>1</sub> )	0.04, 0.06	0.22, 0.23
H(C <sub>2</sub> )	0.05	0.22, 0.23
H(C <sub>3</sub> )	0.05, 0.08	0.22, 0.28
H(C <sub>4</sub> )	0.04	0.29
H(N <sub>1</sub> )	0.16, 0.17	0.31, 0.32
H(N <sub>2</sub> )	0.16	0.43
H(C <sub>5</sub> )	0.06 - 0.07	0.24 - 0.28
H(C <sub>6</sub> )	0.05 - 0.07	0.29



CALCULATED ELECTROSTATIC POTENTIAL OF 1,2-DIAMINOETHANE IN A PLANE PASSING THROUGH THE LONE PAIRS OF BOTH NITROGENS. THE PROJECTED POSITIONS OF THE NUCLEI, IN THIS PLANE, ARE SHOWN. DASHED CONTOURS CORRESPOND TO NEGATIVE POTENTIALS; ALL VALUES ARE IN KCAL/MOLE. THE POSITIONS OF THE MOST NEGATIVE VALUES (MINIMA) IN THIS PLANE ARE INDICATED; THE MAGNITUDES ARE:

■ -41.3 KCAL/MOLE

● -84.6 KCAL/MOLE



CALCULATED ELECTROSTATIC POTENTIAL OF 1,2-DIAMINOBUTANE IN A PLANE PASSING THROUGH THE LONE PAIR OF ONE OF THE NITROGENS. THE PROJECTED POSITIONS OF THE NUCLEI, IN THIS PLANE, ARE SHOWN. DASHED CONTOURS CORRESPOND TO NEGATIVE POTENTIALS; ALL VALUES ARE IN KCAL/MOLE. THE POSITION OF THE MOST NEGATIVE VALUE (MINIMUM) IN THIS PLANE IS INDICATED; THE MAGNITUDE IS -86.3 KCAL/MOLE. THE ABSOLUTE MINIMUM IN THIS LONE PAIR REGION IS -96.9 KCAL/MOLE.

TABLE 1. Electrostatic Potential Minima Associated with Nitrogen Lone Pair Regions.<sup>a</sup>

Numbering of Carbons: $\text{H}_2\text{N}-\text{C}_1-\text{C}_2-\text{C}_3-\text{C}_4-\text{NH}_2$	
Molecule <sup>a</sup>	Minimum, kcal/mole
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$	-95.3
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$	-96.9
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{NH}_2$	$\text{N}(\text{C}_1): -97.7$ $\text{N}(\text{C}_4): -105.3$
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{NH}_2$	$\text{N}(\text{C}_4): -102.6$
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\underset{\text{F}}{\text{CH}}-\text{CH}_2-\text{NH}_2$	$\text{N}(\text{C}_4): -100.9$
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{NH}-\text{CH}_3$	$\text{N}(\text{C}_1): -99.1$ $\text{N}(\text{C}_4): -98.9$

<sup>a</sup> The electrostatic potential minimum associated with the nitrogen lone pair in ammonia is -110 kcal/mole [8].